Membrane for water reuse: effect of pre-coagulation on fouling and selectivity

Y. Soffer*, R. Ben Aim** and A. Adin*

*Division of Environmental Sciences, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
**Laboratory of Environmental Engineering Processes, INSA/GPI 31077 Toulouse, France

Abstract Membrane filtration is adequate for producing disinfected clear water suitable for various kinds of applications. However, fouling of membranes is the main limitation. This study has focused on the ability of flocculation to remove from wastewater the organic colloids which play an important role in the fouling phenomena. First, flocculation was optimized for high-efficiency removal of suspended solids and organic material, and then, at a selected ferric chloride dose and pH, was used as a first step before filtration on membranes ranging from UF (50 KDa) to NF. This resulted in an improvement of the filtration flux. Fouling increased when high molecular weight cut-off (MWCO) membranes were used. The fouling mechanism seems to be blocking, by internal clogging and cake formation becoming preponderant with time. pH 5.5 (charge neutralization zone) provided better removal and lower fouling intensity than pH 7.8 (sweep coagulation zone). Ultrafiltration of 4 KDa at acidic pH 5.5 and 150 mg/L ferric chloride could reduce DOC by 70% and UV-254 nm by 60%. The quality of the filtrate was better than that obtained with nanofiltration at basic pH 7.8 with the same dose of flocculant and the fouling was lower with a 4 KDa membrane. Thus coupling of flocculation with a UF membrane might be the best compromise for producing, in very compact units, very clear water for possible reuse in industrial areas.

Keywords Ultrafiltration; fouling; selectivity; membrane filtration; physical-chemical treatment; flocculation; iron coagulation; advanced wastewater treatment; water reuse

Introduction Membranes are sensitive to the fouling phenomenon resulting in a decrease in filtrate flux. In-line flocculation-membrane filtration is a method which reduces the degree of internal clogging. Flocculation is used to reduce penetration of colloidal particles or organic matter into membrane pores and to modify deposit characteristics (Ben Aim et al., 1988). Lahoussine-Turcaud et al. (1990a) found that iron coagulation of surface water was the most efficient for reducing fouling phenomena, when flocculation conditions produced particles with zeta potential close to zero. This is thought to be due to the differences in particle size and cake porosity. Lahoussine-Turcaud et al. (1990b) investigated filtration (1 KDa) of tannic acid, humic acid and kaolin: particles near 0.2 µm in diameter produced rapid fouling, and particles greater than 3 µm had little effect on the flux. The fouling behavior of humic substances after coagulation with polyaluminium chloride depends on pH (Lahoussine-Turcaud et al., 1992): for pH<7, fouling is lower than for pH>7. The main phenomenon controlling the filtrate flux is the formation of a cake on the membrane, while for pH<7 some internal fouling occurs as well.

The scope of the present study is to examine the effect of iron coagulation of primary wastewater effluent on membrane filtration. The ability of iron coagulation to improve the removal of dissolved organic matter was tested in parallel to fouling characterization at different MWCO, dose-pH, with or without floc separation prior to filtration.

Materials and method Membrane filtration tests. A 500 cm³ pressurized stirred cell was fitted with 75 mm diameter membrane discs (Table 1). Stirring rate was 500 rpm, and 3 · 10⁵ Pa transmembrane pressure was maintained for UF membrane and 6 · 10⁵ Pa for NF (nanofiltration). Samples for
turbidity, UV-254 nm and DOC were collected. The filtrate flux was measured by weighing out samples on a balance (Sartorius basic 3100, ±0.01 g). All experiment runs ended after 345 ml of wastewater were filtered. Membrane influent was primary municipal wastewater effluent after coagulation with ferric chloride (FeCl₃ · 6 H₂O) at two different pH levels: 7.8 (natural) and 5.5. Flocculation was performed using conventional jar test procedure. Three kinds of samples were filtered: wastewater without coagulant (wc), suspension obtained after flocculation without settling (ws), and supernatant after settling (as). The influence of the deposit formed on the membrane was evaluated by simple water rinsing and measurement of the permeability. After the filtration test, the membrane was cleaned by soaking at ambient temperature for 12 hours in a NaOH solution. The variation of average pure water flux with different membrane discs was within 4% of the average value. All fouling curves (J/Jₒ) are reported with viscosity corrections to 20ºC (J-the permeate flux at time t, Jₒ – the permeate flux of clean membrane).

Wastewater. The raw wastewater used in this study was directly pumped into a sewer crossing the campus of INSA-TOULOUSE and allowed to settle for three hours. The characteristics of this primary effluent are the following: turbidity: 52–60 NTU; UV-254 nm: 0.4–0.45 cm⁻¹; DOC: 112–125 mg/L; Zeta potential: –27– – 31 mV; TSS: about 140 mg/L; COD: about 380 mg/L; COD (soluble): about 160 mg/L; pH: 7.8–7.9.

Analytical procedure. The efficiency of coagulation and membrane filtration was determined by monitoring turbidity, DOC (dissolved organic carbon, Ionics-1555B) and UV-254 nm absorbance representative of humic-like organic matter (Backman D-40). Except for turbidity measurement, samples were filtered through a 0.45 µm membrane. Zeta potential was measured by Malvern Zeta Master.

Results and discussion

Jar test. The efficiency of coagulation at various coagulant dosage is shown in Figures 1 and 2, for two different pHs: 7.8 (natural pH) and 5.5. All C/Cₒ values are positive, except for UV-254 nm absorbance at pH 5.5 in the case of insufficient coagulant dose and overdose. This “negative effect” may be due to the sensitivity of the UV-254 nm absorbance measurement to small colloids. At pH 5.5, the optimal dose was between 150 and 200 mg/L, whereas, at pH 7.8 the efficiency increases with the dose up to 300 mg/L. At 150 mg/L the C/Cₒ values are lower at pH 5.5 than at pH 7.8. At this dose, the improvement in colloids removal (turbidity) was higher than that of the DOM (dissolved organic matter – which is represented by UV-254 nm and DOC). In contrast to the basic pH (sweep coagulation zone), the high existence of positive soluble iron species and positive iron hydroxide at acidic pH increased the probability of adsorption and charge neutralization interactions with DOM. The better efficiency obtained at a lower pH is explained by the fact that the humic substances become more hydrophobic and less negatively charged when decreasing the pH. At a low pH the

<table>
<thead>
<tr>
<th>Membrane characteristics</th>
<th>H₂O (KDa)</th>
<th>Material</th>
<th>Permeability (L/h·m²·bar) 20ºC</th>
<th>pH resistance</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF - PA 50 H</td>
<td>50</td>
<td>Polyamide (PA)</td>
<td>570</td>
<td>1–12</td>
</tr>
<tr>
<td>UF - C 30</td>
<td>30</td>
<td>Cellulose (C)</td>
<td>70</td>
<td>1–12</td>
</tr>
<tr>
<td>UF - C 10</td>
<td>10</td>
<td>Cellulose (C)</td>
<td>21</td>
<td>1–12</td>
</tr>
<tr>
<td>UF - PES 4 H</td>
<td>4</td>
<td>Polyethersulfone (PES)</td>
<td>10</td>
<td>1–14</td>
</tr>
<tr>
<td>NF - N 30 FP</td>
<td>–0.6</td>
<td>Polyethersulfone (PES)</td>
<td>3.5</td>
<td>4</td>
</tr>
</tbody>
</table>

* manufactured by CELGARD (NADIR types)
degree of complexation of humic material with iron is high. Comparing Figures 1 and 2, it can be seen that the decrease of pH with ferric chloride addition is higher when the initial pH is lower.

Membrane filtration without flocculant. Tests at various MWCO (4–50 KDa) were performed in order to find the MWCO influence on the efficiency of water treatment (Figure 3a) and on fouling intensity (J/Jo – fraction of initial flux) as a function of filtration time (Figure 3b). For both pH values, a decrease in MWCO value results in higher removal efficiency except for turbidity removal with a 50 KDa membrane. The nature of the membrane material and the conditions of operation (dead end filtration, without agitation in this case) could explain this result. The efficiency in UV absorbance removal (representative of aromatic compounds) is quite small and independent of the pH. However, DOC removal is quite high at pH 5.5. It can be assumed that for pH 7.8, the influence of physical separation is higher than the physical-chemical interaction (most of the organic materials have an acidic iso-electric point which affects the size and charge). Concerning fouling (rate of decreasing of J/Jo) it can be seen from Figure 3b that it is nearly independent of pH and strongly dependent on MWCO. The fouling rate is more rapid with increasing the MWCO (for 30–50 KDa than for 4–10 KDa). Since the DOM removal for membrane with high MWCO is low, it may be assumed that the origin of the high flux decline rate when starting the run is caused by pore blocking (immediate process). In that case the effect of adsorption-polarization (fast process) is less significant (major mechanism for 4–10 KDa). For filtration testing with high MWCO (50 KDa) the contribution of the cake layer to membrane resistance is higher (32–50% at terms of difference in J/Jo before and after surface wash) compared with smaller pore size membranes. This can be attributed to the activity of a back transport mechanism.

Membrane filtration of wastewater after iron coagulation. As the optimal dose of flocculant is high (>300 mg/L at initial pH 7.8) experiments have been performed for examining at the influence of smaller doses (25 and 75 mg/L). In these conditions after coagulation, the suspension was filtered on a 50 KDa membrane with or without previous settling. As seen in Figure 4a, the effect of coagulant is significant only at the beginning of the filtration run: after 30 minutes the filtrate flux is the same (=0.05 · J0), independent of the doses and of the process settling. Concerning DOC removal the results are different (Figure 4b): the removal efficiency is increased from 10% to 30%, in the presence of small coagulant doses.
This may be attributed to a gel layer whose rate of formation is dependent on the coagulant dose.

**Membrane filtration using MWCO of 10 KDa.** Variation in DOM removal applying the optimal dosage from the jar test (150 mg/L) at pH 5.5 and comparing with the same dose at pH 7.8 is shown in Figure 5a. With 10 KDa, using the optimum conditions for coagulant (150 mg/L; pH 5.5) is necessary for minimizing the fouling and obtaining a stabilized filtrate flux. The presence of the flocs is not favorable (Figure 5a). Concerning UV-254 nm absorbance and DOC removal (Figure 5b), at pH 5.5, the membrane alone is only slightly more efficient than coagulation settling. However, coupling allows both an improvement in efficiency (=15% increment for DOC and =10% increment for UV-254 nm).
Membrane filtration using MWCO of 4 KDa. As shown in Figure 6a the fouling is limited. The addition of coagulant improves the results only slightly and only in the case of previous separation of the flocs. The influence of pH is hardly detectable in this case. This influence is more significant on the removal efficiency (Figure 6b). Concerning UV removal, similar results are obtained by the membrane alone at pH 7.8 and on the jar test at pH 5.5. Coupling of both processes gives a substantial increase of removal efficiency: >75% for DOC and >50% for UV at pH 5.5, H3336170% for DOC and H3336160% for UV at pH 7.8. So in the case of this membrane, coagulation at natural pH (7.8) with ferric chloride at a dose of 150 mg/L is an adequate pretreatment for good conditions of operation (low fouling; acceptable retention).

Comparison between low MWCO UF membrane and NF with ferric chloride coagulation-pH 7.8. Surprisingly, the results obtained with the NF membrane are not better than those obtained with the UF membrane (MWCO 4 KDa). In similar conditions the relative fouling is more important (Figures 7a, b). This may be due to the fraction of small molecules

---

Table 2  Comparison between jar test and filtration effluents

<table>
<thead>
<tr>
<th></th>
<th>Respective contribution of internal fouling (Ji/J0) and deposit (Jd/J0) on flux decrease</th>
<th>UV-254 nm removal ratio (after filtration/jar test)</th>
<th>DOC removal ratio (after filtration/jar test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-10 KDa (pH 7.8)</td>
<td>1%/25%</td>
<td>4%</td>
<td>74%</td>
</tr>
<tr>
<td>UF-10 KDa (pH 5.5)</td>
<td>2%/13%</td>
<td>15%</td>
<td>85%</td>
</tr>
<tr>
<td>UF-4 KDa (pH 7.8)</td>
<td>1%/17%</td>
<td>6%</td>
<td>82%</td>
</tr>
<tr>
<td>UF-4 KDa (pH 5.5)</td>
<td>5%/11%</td>
<td>45%</td>
<td>84%</td>
</tr>
<tr>
<td>NF-N-30F (pH 7.8)</td>
<td>30%/14%</td>
<td>215%</td>
<td>56%</td>
</tr>
</tbody>
</table>
present in the primary effluent and partially retained by the NF membrane with consecutive fouling. Due to this higher resistance the NF membrane is not affected by floc deposits: the main resistance increase is due to internal fouling as shown in Table 2. Concerning UV-254 nm or DOC removal, the NF membrane is only slightly more efficient than the 4 KDa UF membrane.

Summary and conclusion
1. Pre-coagulation significantly affects membrane fouling and separation, particularly at an optimum dose, pH condition. Coagulation at pH 5.5 can remove 56%-DOC and 35%-UV-254 nm absorbance by adsorption and charge neutralization mechanism. For a higher pH, where sweep coagulation mechanism prevails, removal is only 11% and 15%, respectively.

2. In filtration without flocculant, the lower the UF-MWCO, the higher is the DOM removal at both pH. Similar to the jar test, DOC removal is higher than UV absorbance. The removal efficiency is higher at pH 5.5 than pH 7.8. MWCO effect on fouling is more pronounced than the pH. The fouling increases with MWCO between 4 KDa and 50 KDa. However, the NF membrane tested was more sensible to fouling due to partial retention of small molecules present in the effluent with or without coagulation.

3. Concerning the UF membrane, the higher the coagulation degree before the membrane, the lower the fouling. At natural pH (pH 7.8), the DOM removal ratio (after filtration/jar test) is more than double compared with pH 5.5. This is why the fouling is higher at pH 7.8 than at pH 5.5 (by 14% for 10 KDa) for both operation modes (with or without flocs).

4. UF cannot compensate for low coagulation level. At this point, the removal efficiency for the entire process is higher at pH 5.5 for both operation modes. For each pH, the operation mode has a significant effect on the fouling level rather than on DOM removal.

5. Turbidity cannot be a sensitive qualitative index for comparison (<0.112 NTU in all filtration tests).

6. DOC removal from primary effluents by physicochemical processes implies a high dose of flocculant and low MWCO (about 4 KDa) due to the nature of the DOM present in the effluent.

Acknowledgements
This work was partially supported by a grant from the French and Israeli Ministries of Science and Technology (AFIRST program). The samples of membranes were kindly provided by CELGARD. This paper is part of graduate work by Y. Soffer.

References

